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Chemical Kinetics: NOx Mechanisms

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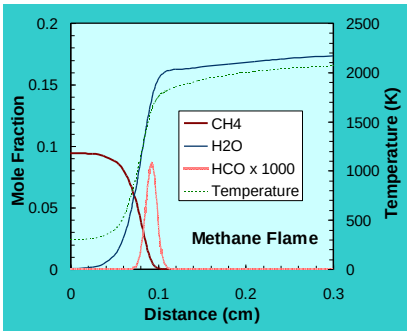

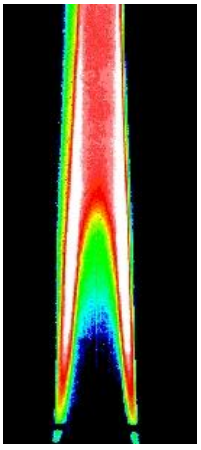

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Overview

- Having now examined mechanisms for fuel oxidation (H_2, CO and HC), the goal here is to revisit mechanisms for NO_x production:
  1. thermal mechanism (extended Zeldovich) for high T, lean conditions
  2. N_2O mechanism for low T, lean conditions
  3. NNH mechanism for high T, stoich/rich, H_2
  4. Fenimore/prompt mechanism for hydrocarbon fuel-conversion zones
  5. NO_2 mechanism for $NO \rightarrow NO_2$ conversion in low T regions

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NOx Formation

- NO_x (NO, NO_2, NO_3) important pollutant
  - NO_2 leads to acid rain/photochemical smog/O_3
  - combustion NO converted to NO_2 in atmosphere
  - can also directly impact human health
- Observation: original Zeldovich mechanism does not accurately predict NO production in
  - wet air
  - low *T* combustion with long residence times
  - stoichiometric and rich H_2-air flames
  - low residence time or rich hydrocarbon flames
- Need more advanced NO mechanisms

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Thermal NO Mechanism

- Already described basic Zeldovich mechanism
  - add reaction for "wet" systems (*H* species)

Extended Zeldovich Mechanism

		ΔH_R
$N_2 + O \leftrightarrow NO + N$	$\{NO.1\}$	+75.1 *kcal/mol*
$O_2 + N \leftrightarrow NO + O$	$\{NO.2\}$	– 32.1 *kcal/mol*
$OH + N \leftrightarrow NO + H$	$\{NO.3\}$	–48.7 *kcal/mol*

- **Thermal NO Formation**
  - still rate limited by { *NO*.1f }
  - dominates at high T (≳1800K), lean environments
  - long τ_{res} usually required (postflame gases)
  - superequilibrium [*O*], [*OH*] increases NO prod. rate

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Intermediate N_2O Mechanism

- N_2 first converted to N_2O then NO

$$N_2 + O(+M) \leftrightarrow N_2O(+M) \quad \{NO.4\} \quad -40\ kcal/mol$$
$$N_2O + H \leftrightarrow NO + NH \quad \{NO.5\} \quad +35\ kcal/mol$$
$$N_2O + O \leftrightarrow NO + NO \quad \{NO.6\} \quad -36\ kcal/mol$$

compete with N_2O *destruction via*

$$N_2O + H \leftrightarrow N_2 + OH \quad \{NO.7\}$$
$$N_2O + O \leftrightarrow N_2 + O_2 \quad \{NO.8\}$$
$$N_2O + OH \leftrightarrow N_2 + HO_2 \quad \{NO.9\}$$

- **NO Formation**
  - $\{NO.4\}$ has Lindemann-like p dependence ($k_0 \rightarrow k_\infty$)
  - medium to high activation energies
    - $E_a(kcal/mol) \sim 18\{NO.4\}; 35\{NO.5\}; 23\{NO.6\}$
  - important in low T, fuel lean ($\phi \lesssim 0.8$) systems (+ high p)
  - NH from $\{NO.5\}$ can also lead to NO

$$NH + O \rightarrow NO + H \quad \{NO.10\} \qquad NH + O_2 \rightarrow NO + OH \quad \{NO.11\}$$

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NNH Mechanism

- Thermal + nitrous mechanisms "ok" for H_2-air, BUT
- NO also produced via NNH intermediate

$$N_2 + H(+M) \leftrightarrow NNH(+M) \quad \{NO.12\} \quad +6.5\ kcal/mol$$
$$NNH + O \leftrightarrow NO + NH \quad \{NO.13\} \quad -11.3\ kcal/mol$$

- $\{NO.13\}$ has same products as $\{NO.5\}$
  - and NH can also lead to NO via $\{NO.10$ and $.11\}$
- Where is NNH mechanism (path) important?
  - for $T \gtrsim 2200$ K, important for stoichiometric and rich, low residence time systems, H_2-air flames
  - for $T \gtrsim 1900$ K, most impact (relative to thermal NO_x) near stoichiometric (and at lower T)

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Fenimore/Prompt Mechanism

- In thermal, N_2O, and NNH mechanisms, NO produced via conversion **from attack on** N_2/O_2 **via** radicals containing only N, O, H nuclei
- Sufficient for wet air and hydrogen combustion
- NO can also be produced in **hydrocarbon** combustion via C species
  - **prompt** NOx – Fenimore observed NO formed earlier in HC combustion than possible from thermal mechanism
- General reaction scheme
  - CH_x (e.g., CH, CH_2 and CH_3) radicals react with molecular nitrogen to form HCN (hydrogen cyanide)
  - conversion to NO through various intermediates

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Fenimore Scheme

- Early version of the mechanism
- Rate limiting step

$$CH + N_2 \leftrightarrow HCN + N$$ **conversion of N_2**

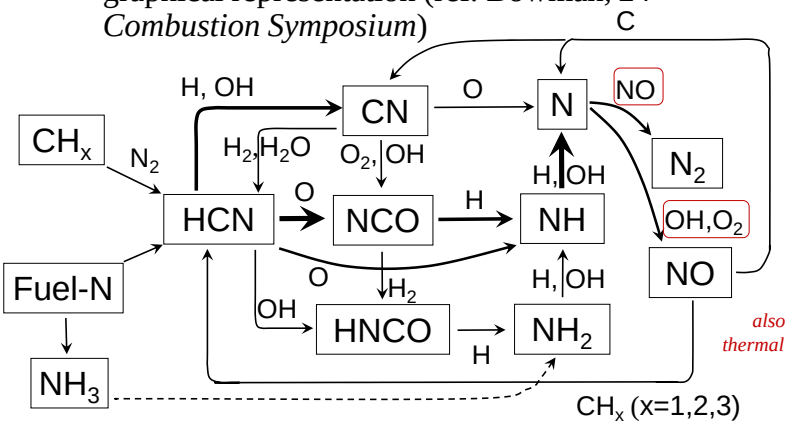
- Conversion to NO

$$HCN + O \leftrightarrow NCO + H$$
$$NCO + H \leftrightarrow NH + CO$$
$$NH + H \leftrightarrow N + H_2$$
$$N + OH \leftrightarrow NO + H$$

  - conversion to NO via radical/radical reactions
- Limited accuracy (e.g., ϕ<1.2)

General Prompt Mechanism

- Many reactions for range of rich mixtures/fuels
  - graphical representation (ref. Bowman, *24th Combustion Symposium*)



also in thermal mech.

NO_2 Mechanism

- Noted that NO converted to NO_2 in atmosphere
  - combustion systems also convert NO to NO_2
    - can sometimes be significant fraction of total combustor NOx emissions $[NO]+[NO_2]$

$$NO + HO_2 \leftrightarrow NO_2 + OH \quad \{NO_2.1\}$$ **HO_2 formed @ low T**

$$NO_2 + H \leftrightarrow NO + OH \quad \{NO_2.2\}$$

$$NO_2 + O \leftrightarrow NO + O_2 \quad \{NO_2.3\}$$

forward reactions (NO_2 recycled to NO) active at high T

- No NO_2 from hot regions
- NO_2 in combustion systems often comes from NO formed in hotter regions mixing into low T regions

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Example: Premixed Laminar Flame

- NO_2, prompt important in *reaction zone*; thermal in downstream